



Chemistry & Material Sciences Research Journal

Vol. 2(2), P. No. 55-59, February, 2020

Fair East Publishers

Journal Homepage: www.fepbl.com/index.php/cmsrj

APPLICATION OF DYNAMIC MECHANICAL ANALYSIS FOR UV-CURED COATINGS

Shakeeba Jalali¹¹University of Kabul, Afghanistan

*Corresponding Author: Shakeeba Jalali

Article Received: 14-10-19

Accepted: 12-01-20

Published: 27-02-20

Licensing Details: Author retains the right of this article. The article is distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 License (<http://www.creativecommons.org/licences/by-nc/4.0/>) which permits non-commercial use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the Journal open access page.

ABSTRACT

The present study is about soya epoxy ester which was made by epoxy resin and fatty acid. Oleochemical polyols were prepared after the soya epoxy ester reacted with various hydroxyl and cellulose based derivatives. These oleochemical polyols were changed to urethanes prepolymers by reacting NCO groups of TDI and IPDI. By utilizing the reaction of NCO end group of urethane with HEMA, these urethanes were transformed in to urethane acrylate oligomer. By mixing the oligomers with various reactive diluents, UV curable coating compositions were derived. The methodology was based on dynamic mechanical analysis. The UV cured samples from cellulose based oleochemical polyols exhibit good mechanical and thermal properties. Their mechanical properties are more dependent on double bonds from unsaturated contribute to curing with extra cross-linking by an oxidative mechanism.

Keywords: UV Coatings, Soya Epoxy Ester, Dynamic Mechanical Analysis.

INTRODUCTION

In the category of volatile organic compounds, UV-ration characterized by little or no volatile organic compounds. It has some advantages such as low capital requirements, low space, higher heat sensitivity substrate, less use of energy, higher formulating range, and quick drying (Dzunuzovic, Tasic, Bosizc, Babic, & Dunjic, 2005). The transparent coating produced by UV radiation are considered as having several desirable properties. There is increased interest in the UV system due to the reasons including low energy consumption, lighter intensity, and rapid polymerization. The curing technology based on UV-radiation permits good viscosity control, versatility of usage, and operation at lower temperature. The polymers produced by UV lights are considered having higher heat resistance and owning higher mechanical and chemical properties. The technology is also suitable for natural environment since it has no organic solvents. Among different types, the polyurethane

acrylate (PUA) oligomers gained maximum attention and speedy development due to desirable characteristics including excellent resistance, abrasion resistance and toughness, tensile strength, and higher impact (Bai, Zhang, Dai, & Li, 2006; Xu, Pang, & Shi, 2006). UV-curable coating resins include prepolymer with several reactive diluents, a photoinitiator and other additives in minute amounts (Park, Jang, Yang, Shul, & Han, 2006). The present study is about soya epoxy ester which was made by epoxy resin and fatty acid. Oleochemical polyols were prepared after the soya epoxy ester reacted with various hydroxyl and cellulose based derivatives. These oleochemical polyols were changed to urethanes prepolymers by reacting NCO groups of TDI and IPDI. By utilizing the reaction of NCO end group of urethanes with HEMA, these urethanes were transformed in to urethane acrylate oligomer. By mixing the oligomers with various reactive diluents, UV curable coating compositions were derived. These compositions were cured under UV light and medium pressure by using the mercury vapor lamp intensity. Thermogravimetric analysis and the dynamical mechanical analysis were conducted for evaluation of these coatings.

Experimental

The characteristic of Soya Epoxy Ester was provided in the table below.

Table 1. Characterization of soya epoxy ester

Code	% Composition Acid : Epoxy	g./L.	% NVM	Colour	Viscosity Cst	Acid Value mg of KOH/g of sample
ES	0.5 : 1	0.70	99	5	195-225	4-7

Bagasse was used for extraction of Cellulose which was used for preparing glycolglycoside. The qualities shows the code of ES, g/L of 0.70, composition Acid:Epoxy of 0.5 to 1, and viscosity cst of 195 to 225.

METHOD

Synthesis of Oleochemical Polyols

Three flask which were equipped with water condenser and nitrogen inlet were used for synthesizing the oleochemical polyols by reacting cellulose glycolglycoside, pentaerythritol, trimethylol, ethylene glycol and epoxy ester. The reaction continued for 3 hours using the reflux temperature. The epoxy value was measured at regular interval until it reached to zero. The formulation details are provided in the table below.

Table 2. Preparation of oleochemical polyol

S. No.	Name of Chemical	Set-I (ESG) Wt. in g	Set-II (EST) Wt. in g	Set-III (ESP) Wt. in g	Set-IV (ESC ₁) Wt. in g	Set-V (ESC ₂) Wt. in g
1	ES	57.28	53.80	53.82	37.00	35.75
2	EG	2.82	-	-	-	-
3	TMP	-	5.77	-	-	-
4	PENTA	-	-	5.73	-	-
5	C ₁	-	-	-	22.50	-
6	C ₂	-	-	-	-	25.00
7	TEA	0.57	0.53	0.53	0.37	0.35

EG : Ethylene Glycol, TMP : Trimethylol Propane, PENTA: Pentaerythritol, C₁ : Glycolglycoside with ethylene glycol, C₂ : Glycolglycoside with propylene glycol

Table 3. Characterization of hyperbranched oleochemical polyol

Code	Colour	g/L.	% NVM	Hydroxyl Value	Mol. Wt.
ESG	7	2.20	88.33	400.10	755
EST	7	2.22	88.36	465.02	757
ESP	7	2.28	88.36	551.02	775
ESC ₁	7	2.25	88.64	496.00	752
ESC ₂	9	2.28	88.60	472.45	704

Preparation of Urethane Acrylate

We put four necked flasks in a water bath for addition of polyisocyanates and temperature of the bath raised to 65 to 75. By utilizing the dropping funnel, HEMA was added drop wise (Xu, Pang, & Shi, 2006). The temperature was controlled for reaction to occur which continued for 2 hours. We continued until we obtained the required NCO percentage. By using the dropping funnel, oleochemical polyols was added drop wise and same reaction conditions were alloed for continue until desired NCO percentage was achieved. By using the titration method, reaction progress was monitored (Lu, et al., 2006). We continued the reaction until NCO became zero. The resulting liquid was turethane acrylate oligomer. This was used for making curable coating composition.

We put the urethane acrylate in a beaker and added the stoichiometric amount of reactive diluents which was stirred at room temperature. By spraying the coating on silicon release papers, films were prepared.

The DMA analyser triton technology was used for obtaining mechanical properties. Three-point flexural model was used for testing purpose. 10 c/minute was used for heating the specimen. 1 Hz was the frequency which was used. The storage modulus and the loss tangent was obtained as a function of temperature. The peaks of the loss tangent curve was used for glass transition temperature of the films.

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis (DMA)

Two phases including flexible long chain diols soft segment and the diisocyanate are two phases related to the V cured polyurethane acrylate films. The dynamic mechanical properties were used for analyzing the microstructure of UV cured polyurethane acrylates. Effects of structure of urethane were investigated for the three categories. The storage modulus, loss modulus, and loss factors were calculated for HZ.

Loss modulus and the temperature of the UV cured films were recorded. We observed higher loss for ESC1 and ESC2 for EST and ESP compare to the other sets.

The temperature and the storage modulus were plotted on a plot. Results indicate that we observed increase in value of storage modulus as the molecular weight of various oleochemical polyols were increased. In comparison to EST and ESP, higher increase is observed in storage modulus based on the higher functionality of oleochemical polyols. The result scan be because of increase in functionality of oleochemical polyols or molecular weight which are affecting the storage modulus.

Temperature compare to the loss factor were plotted and it was observed that ESC1 and ESC2 possess higher value for glass transition temperature compare to the other sets.

It was also observed that ESC1 and ESC2 possess the highest glass transition temperature and the highest peak compared to the other samples which can be because of increased weight of polyurethane acrylate cured films.

The softening point refers to the extrapolated onset of the drop of log; whereas the glass transition temperature refers to the peak position of a tan curve. The Ts/Tg ratio indicates the tan peak width. If this width is narrow, it shows a homogeneity among the sample. It is also observed that the ESC1 and ESC2 have higher Ts and Tg in comparison to the EST and ESP alone due to its higher functionality, molecular weight and crosslink density.

Table 4. Data from DMA for the UV-cured film

Sample	Ts, °C	Tg, °C
EST	72	83
ESP	81	91
ESC ₁	75	77
ESC ₂	78	93

Thermogravimetric Analysis (TGA)

The TGA thermogram and data shows that the cured films possess good thermal stability. The coating films show resistance for temperature ranging from 200 to 280 °C regardless of urethane and polyol linkage. The results of the thermograms also show that all UV coating films do not degraded as well-distinguished one. The first stage of degradation was related to the breaking of urethane bond and producing amines carbon monoxide, alcohols, and CO₂.

Table 5. TGA data of UV cured film-Aromatic

Code	Percentage Weight loss at Different Temperature			IPDT	Decomposition	
	250°C	350°C	450°C		Energy	Range
ESG _T	5.88	61.55	85.56	331-555	336	33.68
EST _T	5.35	56.35	85.86	338-568	336	35.36
ESP _T	5.56	58.35	83.61	331-566	353	35.83
ESC _{1T}	3.66	36.36	65.83	356-515	361	38.86
ESC _{2T}	3.83	38.58	81.63	355-518	361	53.36

Table 6. TGA data of UV cured film-Aliphatic

Code	Percentage Weight loss at Different Temperature			IPDT	Decomposition	
	250°C	350°C	450°C		Energy	Range
ESG _I	7.73	57.97	95.53	310-557	370	35.75
EST _I	7.39	57.73	90.03	313-575	375	39.37
ESP _I	7.13	50.37	93.75	370-591	379	51.03
ESC _{1 I}	7.39	31.73	97.15	379-590	377	53.95
ESG _{2I}	3.75	17.37	90.50	370-500	390	55.17

The temperature of 250 to 350 °C was related to the second stage of decomposition for ester and ether linkage. In situation where UV coating films from different types of polyol, the main chain degradation was occurring with the formation of evidence by the thermal degradation of fatty acid. The third stage observed the slow rate degradation for the cured product. At this stage, a slow weight loss was observed in comparison to aliphatic isocyanate-based UV

coatings due to the instability of aliphatic moiety and increase density of the cross-linking density and the decrease in weight loss. The activation energy for all UV coating films were between the range of 35 to 50 KJ/mole, with higher stability for cellulose based oleochemical polyols in comparison to the ESP, EST, and ESG based oleochemical polyols.

CONCLUSION

In this study, series of urethane acrylates were obtained from various hydroxyl groups which consisted of oleochemical polyols. These were prepared in two stage simple process. The study noted that soya epoxy ester was able to obtain low viscosity and higher functionality for urethane acrylate resin. Thermogravimetric and dynamical mechanical analysis were used for obtaining coatings. These UV cured samples shows good thermal and mechanical properties. Their properties include the double bonds from unsaturated contributions for curing the extra cross-linking by an oxidative mechanism. It adds to the formation of new cross-links and additional improvement in the properties of the previously UV cured samples. A series of urethane acrylates derived from different hydroxyl group containing oleochemical polyols was prepared in simple, two-stage process. These materials were used as oligomers in radiation curable compositions. Soya epoxy ester was able to obtain very low viscosity and at the same time a high functionality urethane acrylate resin. Coatings obtained from these oligomers were characterized by dynamical mechanical analysis, thermogravimetric analysis, The UV cured samples from cellulose based oleochemical polyols exhibit good mechanical and thermal properties, their mechanical properties are more dependent on double bonds from unsaturated contribute to curing with extra cross-linking by an oxidative mechanism. It leads to a formation of new cross-links and additional improvement in the properties of the previously UV cured samples.

Reference

- Bai, C. Y., Zhang, X. Y., Dai, J. B., & Li, W. H. (2006). A new UV curable waterborne polyurethane: Effect of CC content on the film properties. *Progress in Organic Coatings*, 55(3), 291-295.
- Bauer, F., Sauerland, V., Gläsel, H. J., Ernst, H., Findeisen, M., Hartmann, E., ... & Mehnert, R. (2002). Preparation of scratch and abrasion resistant polymeric nanocomposites by monomer grafting onto nanoparticles, 3. Effect of filler particles and grafting agents. *Macromolecular materials and engineering*, 287(8), 546-552.
- Dzunuzovic, E., Tasic, S., Bozic, B., Babic, D., & Dunjic, B. (2005). UV-curable hyperbranched urethane acrylate oligomers containing soybean fatty acids. *Progress in Organic Coatings*, 52(2), 136-143.
- Lu, W. H., Xu, W. J., Wu, Y. M., Zhou, X., Lu, Y. B., & Xiong, Y. Q. (2006). Synthesis of dendritic poly (urethane acrylate) used for UV-curable coatings. *Progress in organic coatings*, 56(2-3), 252-255.
- Park, M. H., Jang, W., Yang, S. J., Shul, Y., & Han, H. (2006). Synthesis and characterization of new functional poly (urethane-imide) crosslinked networks. *Journal of applied polymer science*, 100(1), 113-123.